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(54) Title: PRODUCTION OF POLYESTERS AND POLYESTER ARTICLES HAVING GOOD CLARITY (57) Abstract Disclosed is an improvement in a process for producing linear polyesters wherein a precursor polyester is first formed and subsequently the precursor polyester is formed into particles and further polymerized in the solid state, wherein the improvement comprises contacting the particles while at a temperature of about 140 to about 2 °C below the melting point of the polyester with the vapor of water or an organic compound having at least one OH group.		

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PRODUCTION OF POLYESTERS AND
POLYESTER ARTICLES HAVING GOOD CLARITY

Technical Field

5 The present invention relates to polyesters having improved resistance to the formation of gels when formed into articles, thereby resulting in articles having good clarity. As used herein, the term "polyesters" is intended to mean linear polyesters and copolyesters.

10 The invention is particularly applicable to polyethylene terephthalate (PET).

Background of the Invention

15 Polyesters such as PET of high molecular weights provide certain properties such as toughness, melt strength and slow crystallization rate that are desirable for clear film and extrusion blow molded articles such as beverage bottles. The high molecular weight polyesters are generally prepared by a melt-phase

20 polycondensation process followed by a solid-state polymerization process. When the molecular weight of a polyester increases, the chain length increases resulting in an increase in the tendency for chain entanglement. Areas of high entanglement may be viewed

25 as localized networks of very high molecular weights and are the centers of gels observed on a macro scale upon molding into articles.

 During melt phase polymerization, polymer chains have enough mobility so that localized networks due to

30 entanglement are reduced. On the contrary, during solid-state polymerization, parts of the polymer chains are already engaged in crystalline regions. Therefore, the chains have limited mobility. As the polymerization progresses, 'knots' and 'kinks' are formed. The degree

35 of entanglement is therefore increased leading to the

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formation of localized polymer networks. The entanglements manifest themselves as gels which are often observed upon molding into articles. The greater the difference between solid-state polymerized and melt-phase polymerized molecular weight, the greater the tendency to form gels.

Parts of the polymer chains in the localized polymer networks formed during solid-state polymerization are under excessive strain because of the lack of mobility of the chains. The points along the polymer chain with the highest strains are most vulnerable to chemical attack. If certain molecules are present in the effluent gas during solid-state polymerization, the ester bonds under the greatest strain will be broken the fastest, thus producing a 'relaxing' effect for the networks and entanglement is reduced. As a result, the number of gels is reduced.

Applicants are not aware of any prior disclosures of adding vapor of compounds having reactive OH groups to the effluent gas to produce linear polyesters of high molecular weights that will yield gel-free, high clarity films. In fact, most of the literature advises that moisture should be kept to a minimum to prevent loss of solid-state polymerization rate. There are a few patents that mention use of water/alcohols during solid-state polymerization, but they are irrelevant to the present invention, as explained below. Treatment of poly(ethylene terephthalate) polymers with supercritical carbon dioxide and water under high pressure to reduce acetaldehyde is known. However, both carbon dioxide and high pressure are required and it was not under solid-state polymerization conditions. Swiss Patent Application No. 655,938 discloses a process of two stages: (1) treating the polyester with alcohol or alcohol/water until the aldehyde content is below 35 ppm

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then (2) postcondensing at 200-245°C. It requires the measurement for acetaldehyde at the first stage and is therefore irrelevant to our present invention which applies to polymers without the need of intermediate measurement of acetaldehyde. Japanese Patent No. 59219328 discloses a process to perform moisture conditioning with a moisture content of at least 0.2 wt % to reduce acetaldehyde. The level of water disclosed is much higher than that which our present invention requires and is therefore irrelevant. Japanese Patent No. 55013715 discloses extraction of polyesters before or after solid-state polymerization by dipping the polyesters in solvents. European Patent Application No. 389,948 discloses bringing PET having an intrinsic viscosity of at least 0.50 dl/g and a density of 1.38 or more into contact with water to reduce the amounts of oligomers and acetaldehyde formed at the time of molding.

The present invention involves contacting the precursor polyester particles with the vapor of water or an organic compound having one or more hydroxyl groups, preferably into the effluent gas during or after solid-state polymerization of polyesters or during crystallization.

25

Description of the Invention

According to the present invention, in a process for producing linear polyesters wherein a precursor polyester is first formed and subsequently the precursor polyester is formed into particles and further polymerized in the solid state, the improvement is provided which comprises contacting the particles while at a temperature of about 140 to about 2°C below the melting point of the polyester for a time of about 0.1

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to about 100 hours with the vapor of water or an organic compound having at least one OH group.

According to a preferred embodiment of the present invention, in a process for producing linear polyesters wherein a precursor polyester is first formed and subsequently the precursor polyester is formed into particles and further polymerized in the solid state, there is provided the improvement which comprises contacting the particles while at a temperature of about 140 to about 2°C below the melting point of the polyester for a time of about 1 to about 100 hours with inert gas having a flow rate of greater than 2×10^{-2} meters per second, the inert gas containing about 300 to about 7000 parts per million by volume of the vapor of water or an organic compound having at least one OH group.

Normally, in continuous solid stating of polyesters, the precursor is crystallized under forced motion at a temperature of 100°C to 260°C under an atmosphere of inert gas, air or mixture of inert gas and air. It is then passed to a continuous fixed bed reactor, and continuously polycondensed in the reactor while in contact with an inert gas stream.

Further, according to the present invention, there is provided a process for producing polyester articles having improved clarity and reduced gel content which comprises

- a) producing a polyester having an I.V. of about 0.3 to about 1.0 by the melt phase polymerization of at least one dicarboxylic acid or corresponding ester such as the dimethyl ester having 3 to 22 carbon atoms and at least one glycol having 2 to 18 carbon atoms,

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- b) forming particles of the polyester to a size, expressed in weight, of about 0.002 g/particle to about 0.2 g/particle,
- c) contacting the particles while at a temperature of about 140 to about 2°C below the melting point of the polyester for a time of about 0.1 to about 100 hours with the vapor of water or an organic compound having at least one OH group,
- d) heating the particles to form a melt and
- e) molding the melt into an article.

It is preferred that the vapor described herein be mixed with or injected into the inert gas which is conventionally used in solid stating processes. However, the polyester particles may be contacted by the vapor alone. If the vapor is pure or used in high concentrations, the contact time may be short within the range stated above. However, if the vapor is used in low concentrations, the contact time is long within the range stated above. Thus, the contact time required is inversely proportional to the concentration or purity of the vapor. Because of the obvious advantages of mixing the vapor with the inert gas used in conventional solid stating processes, this specification will refer, in the most part, to such processes wherein the vapor is mixed with the inert gas. Thus, a separate processing step is not required.

The point of introduction of the vapor can be anywhere along the process of a continuous solid-state polymerization. That is, the point of introduction can be at the bottom of the reactor, close to the top of the reactor or any point in between in a continuous process. It can even be at the end of the solid-state polymerization by treating the particles with vapor in a reactor at the end of the solid-state polymerization process. It can also be anywhere along the reaction

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profile in a batch process. That is, vapor can be added at the beginning, towards the end or anywhere in between in a batch process.

5 The vapor can be added as a continuous stream or in pulses. The vapor can also be introduced into the process at more than one location simultaneously, continuously or in pulses. In the latter case, the pulses at the different locations can be synchronized or staggered.

10 The precursor polyester usually has an I.V. of about 0.3 to about 1.0, most often about 0.5 to about 0.8 dl/g. The precursor polyester is typically made by conventional, well known techniques of esterification or transesterification of one or more dicarboxylic acids or
15 corresponding esters with one or more glycols, followed by condensation to a low molecular weight, or precursor polyester.

While the present description is concerned to a large extent with the preparation of polyethylene
20 terephthalate by reason of the commercial importance of this material, the method is also suitable for the treatment of similar homopolymers and copolymers. These may be exemplified by the crystallizable homo- and copolymeric esters of terephthalic, isophthalic,
25 chloroterephthalic, nitroterephthalic or hydrogenated terephthalic acids with one or more glycols, such as ethylene glycol, propylene glycol, 2,2-dimethyl-
propanediol-1,3, 1,4-butane glycol and 1,4-cyclohexane-
dimethanol, as well as copolymers of the type which may
30 be derived from one or more of those glycols and a plurality of acids comprising (1) substituted and unsubstituted terephthalic acids as just described and also (2) one or more of such acids as adipic, sebacic or
2,6-naphthalene dicarboxylic acids. For instance,
35 suitable copolyesters may be prepared from terephthalic

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acid and a mixture of ethylene glycol and
1,4-cyclohexanedimethanol or from ethylene glycol,
diethylene glycol and a mixture of a major proportion of
terephthalic acid and a minor proportion of isophthalic
5 acid. The polyesters prepared in accordance with the
present invention are not limited to those prepared from
such glycols and acids per se, for other preparatory
methods are usually suitable as exemplified by the
esterification of terephthalic acid with alkylene
10 oxides, such as ethylene oxide, or the
transesterification of dimethyl terephthalate with
ethylene glycol.

The dicarboxylic acid(s) or corresponding esters
and glycol(s) are reacted in well known manners to form
15 the polyester precursor. Any of the well known,
conventional catalysts such as, but not limited to, Mn,
Ti, Zn, Ge, Sb, Co, and P, may be used to form the
polyester in accordance with the present invention. For
example, see U.S. Patents 4,010,145 and 3,962,189. The
20 precursor pellets are produced by forming solid
particles, normally pellets, from the precursor polymer
in well known manner.

The polyester precursor particles are normally
crystallized under forced motion at a temperature of
25 about 100°-260°C prior to being solid-state polymerized.
In some processes, the crystallization and solid-state
polymerization steps might not be distinct.

Normally, in solid stating pellets in accordance
with the present invention, particles of regular or
30 irregular shape may be used. The particles may be of
various shapes and sizes such as spherical, cubical,
irregular such as described in U.S. Patent No. 5,145,742
(incorporated herein by reference), cylindrical, or as
described in U.S. Patent No. 4,064,112. "Particles"
35 also includes shapes which are generally flat.

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Solid-state polymerization is a process well known in the art. See, for example, U.S. Patent No. 4,064,112, which is incorporated herein by reference. Generally when molding grade pellets are produced, either a batch or continuous process is used. Continuous processes are preferred for commercial operations for obvious reasons.

Solid stating is normally accomplished by subjecting the polyester particles to a temperature of about 140° to about 2°C, preferably about 180°-10°C, below the melting point of the polyester. The time of solid stating can vary over a wide range (about 1 to 100 hours) according to temperature to obtain the desired I.V., but with the higher temperatures, usually about 10 to about 60 hours is sufficient to obtain the desired I.V. or molecular weight. During this period of solid stating, it is conventional to flow a stream of inert gas through the pellets to aid in temperature control of the polyester pellets and to carry away reaction gases such as ethylene glycol and acetaldehyde. Nitrogen is especially suitable for use as the inert gas because it contributes to the overall economy of the process. Preferably, the inert gas is recycled for economic reasons.

Other inert gases which may be used include helium, argon, hydrogen, and mixtures thereof. It should be understood that the inert gas may contain some air.

Some solid-state polymerization processes use air or mixture with inert gases particularly during crystallization. Our invention also applies to these processes.

By the term "flowing the inert gas through the particles", or similar expressions herein, it is meant moving an atmosphere containing the inert gas, which in turn contains the water or organic compound described

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herein, through the particles for a time of about 0.1 to about 100 hours, preferably about 10-60 hours, at a temperature at which the organic compound is in a vaporous state. Preferably, this is accomplished by
5 injecting the water or organic compound into the inert gas used in solid stating.

According to the present invention, vapor of water or an organic compound having reactive OH groups is preferably mixed with or injected into the inert gas.
10 While this may be done during solid stating or subsequent to solid stating, it is preferred that vapor be mixed with or injected into the inert gas used during solid stating. The vapor used may be mixed with the inert gas as vapor, or as a liquid which will quickly
15 vaporize when it is contacted by the inert gas. The inert gas and polyester particles should be at a temperature sufficiently high to maintain the vapor in the vapor state throughout the solid stating process.

The amount of vapor used is between 300 and 7,000 parts per million (ppm) parts inert gas by volume in
20 conventional solid stating processes. Preferably about 500 to about 2,000 ppm are used. When a separate step is used, either non-diluted vapor or vapor diluted with inert gas to at least 300 ppm vapor content is used. As
25 mentioned previously, the inert gas may contain some air.

Water is the preferred compound containing at least one reactive OH group. Other organic compounds which may be used include methanol, ethanol, propanol and
30 ethylene glycol. As a practical matter, the organic compounds will contain no more than 4 hydroxyl groups.

The vapor is thoroughly mixed with the inert gas prior to flowing through the particles. This may be accomplished by conventional mixers or injectors located
35 in the inert gas conduit just prior to entering the

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solid stating vessel. Typical mixing apparatus or processes useful in this invention are well known in the art. For example, the mixing may be accomplished simply by feeding the vapor through a conduit into the inert gas stream:

Preferably a flow rate of greater than 2×10^{-2} m/s, preferably greater than about 8×10^{-2} m/s is used for the inert gas.

The particles used in accordance with the present invention may be molded using conventional procedures. Melting the particles and forming a molded article may be accomplished by apparatus and procedures known in the art, such as, for example, in an extrusion blow molding machine, stretch blow molding machine, injection molding machine, or film casting apparatus (see, for example, U.S. Patent No. 5,149,485 incorporated herein by reference). Preferably, the particles are three-dimensional pellets.

The following examples are submitted for a better understanding of the invention.

Example 1 - A stream of nitrogen (flow rate at 13.3 scfh), was mixed with another stream of moisture-laden nitrogen (flow rate at 0.7 scfh), and was applied to a batch solid-state polymerization reactor through a mix tank. This nitrogen stream had a dew point of $-19 \pm 0.5^\circ\text{C}$. The nitrogen was heated to 215°C with a heat exchanger. The reactor was heated to 215°C . Poly(ethylene co-1,4-dimethylenecyclohexane 96.1:3.9 terephthalate, 850 g, inherent viscosity 0.626 dl/g, precrystallized at 180°C for 60 minutes) was added. The sample was thus solid-state polymerized for 40 hours. The resulting product had an inherent viscosity of 0.861 dl/g. The product was extruded on a Killion extruder with a 1-inch screw to yield a gel-free film of high clarity.

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Example 2 - Polyester precursor pellets having an I.V. of 0.626 are continuously fed into the top of a continuous reactor and removed from the bottom in a manner such that the pellets form a slowly moving bed in which the pellets have a residence time of 54 hours. The size of the reactor is 12 feet in height and 2 feet in diameter. Temperature of the pellets entering the top is 210°C and temperature of the pellets being removed is 220°C. Nitrogen is caused to enter the reactor near the bottom through a circumferential supply ring, and is removed from the top through a conduit. The nitrogen is recycled in conventional manner. The nitrogen temperature entering the reactor is 220°C and the nitrogen temperature leaving the reactor is 214°C. The flow rate is 23 scfh. Water vapor at a temperature of 160°C is injected into the nitrogen stream prior to entering the supply ring in an amount such that the concentration of water vapor is 1050 ppm by weight based on the weight of nitrogen. Pellets being removed from the reactor have an I.V. of 0.93 dl/g. These pellets are subsequently extruded, into a 10 mil film, using a conventional extruder and found to be substantially gel-free by visual inspection.

Example 3 - Example 2 is repeated. Reactor size, nitrogen flow rate, residence time, and water vapor concentration are varied as shown in the following table. I.V. of the solid stated polymer is about 0.93 dl/g in each case. Substantially gel free films, by visual inspection are produced.

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		Reactor Size Height x Diameter, ft	<u>N₂ Flow Rate</u>	<u>Residence Time, Hr</u>	<u>Water Vapor, ppm</u>
5	Example 3	11 x 1	4 scfh	37.8	300
	Example 4	11 x 1	4 scfh	60.5	2500
	Example 5	12 x 2	23 scfh	49.4	1600

10 As used herein, the inherent viscosity (I.V.) is measured at 25°C using 0.50 g of polymer per 100 mL of a solvent consisting of 60% by weight phenol and 40% by weight tetrachloroethane.

15 As used herein, SCFH means standard cubic feet per hour and SCFM means standard cubic feet per minute.

 Unless otherwise specified, all parts, percentages, ratios, etc., are by weight.

20 Obviously, numerous modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described herein.

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CLAIMS

We claim:

- 5 1. In a process for producing linear polyesters
 wherein a precursor polyester is first formed and
 subsequently the precursor polyester is formed into
 particles and further polymerized in the solid
10 state, the improvement characterized by contacting
 the particles while at a temperature of about 140
 to about 2°C below the melting point of the
 polyester for a time of about 0.1 to about
 100 hours with the vapor of water or an organic
 compound having at least one OH group.
- 15 2. In a process for producing linear polyesters
 wherein a precursor polyester is first formed and
 subsequently the precursor polyester is formed into
 particles and further polymerized in the solid
20 state, the improvement characterized by contacting
 said particles while at a temperature of about 140
 to about 2°C below the melting point of the
 polyester for a time of about 0.1 to about
 100 hours with inert gas having a flow rate of
25 greater than 2×10^{-2} meters per second, said inert
 gas containing about 300 to about 7000 parts per
 million by volume of the vapor of water or an
 organic compound having at least one OH group.
- 30 3. In a process according to Claim 1, the improvement
 which comprises simultaneously contacting said
 particles with said inert gas while solid state
 polymerizing said particles.

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4. In a process according to Claim 1, the improvement which comprises first solid state polymerizing said particles, and then contacting said particles with said inert gas.

5

5. A process according to Claim 1 wherein said polyester contains repeat units from at least 60 mol % terephthalic acid and at least 60 mol % ethylene glycol.

10

6. A process according to Claim 1 wherein said precursor polyester has an I.V. in the range of about 0.3 to 1.0 dl/g.

15

7. A process according to Claim 1 wherein said polyester particles are subjected to a temperature of about 140 to about 2°C below the melting point of the polyester for a time of about 1 to about 100 hours to achieve an I.V. of about 0.6 to about 1.6 dl/g.

20

8. A process according to Claim 1 wherein said inert gas is selected from nitrogen, helium, argon, hydrogen, air or mixtures thereof.

25

9. A process according to Claim 1 wherein said inert gas contains about 500-2000 parts per million by volume of the vapor of water or an organic compound containing at least one OH group.

30

10. A process according to Claim 1 wherein said organic compound is selected from the group consisting of methanol, ethanol, propanols and ethylene glycol.

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11. A process according to Claim 1 wherein said vapor is water vapor.
12. A process according to Claim 1 wherein said pellets
5 are subjected to a temperature of about 180°C to about 10°C below the melting point of the polyester.
13. A process according to Claim 1 wherein said inert
10 gas has a flow rate of at least 12×10^{-2} m/s.
14. A process according to Claim 1 wherein said precursor has an I.V. in the range of about 0.5 to about 0.8 dl/g.
15
15. A process according to Claim 1 wherein said polyester pellets contain a catalyst residue.
16. A process according to Claim 1 wherein the vapor of
20 water or an organic compound having at least one OH group is applied as a continuous stream or in pulses.
17. A process according to Claim 1 wherein said vapor
25 is added in a plurality of locations.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 94/00027

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C08G63/80

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 C08G C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,H,T887005 (KIBLER ET AL) 1 June 1971 see the whole document ---	1-10, 12-14
X	DE,A,25 03 000 (GENERAL ELECTRIC COMPANY) 21 August 1975 see claims 1-6 ---	1-9, 12-15
A	FR,A,2 306 227 (GENERAL ELECTRIC COMPANY) 29 October 1976 see claims 1-12 ---	1-10, 12-15
A	EP,A,0 174 899 (THE GOODYEAR TIRE & RUBBER COMPANY) 19 March 1986 see claims 1-10 ---	16
A	US,A,3 453 240 (PLASTER ET AL) 1 July 1969 see claims 1-5 -----	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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